



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01F 11/18		A1	(11) International Publication Number: WO 96/23728 (43) International Publication Date: 8 August 1996 (08.08.96)
<p>(21) International Application Number: PCT/FI96/00058</p> <p>(22) International Filing Date: 30 January 1996 (30.01.96)</p> <p>(30) Priority Data: 950411 30 January 1995 (30.01.95) FI</p> <p>(71) Applicant (for all designated States except US): KAUTAR OY [FI/FI]; T-linja 38 A, FIN-37800 Toijala (FI).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (for US only): VIRTANEN, Pentti [FI/FI]; T-linja 38 A, FIN-37800 Toijala (FI).</p> <p>(74) Agents: LAINE, Seppo et al.; Seppo Laine Oy, Lönnrotinkatu 19 A, FIN-00120 Helsinki (FI).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	
<p>(54) Title: PROCESS AND APPARATUS FOR PREPARING CALCIUM CARBONATE</p> <p>(57) Abstract</p> <p>The present invention concerns a process and an apparatus for preparing calcium carbonate. The process comprises reacting a calcium oxide raw material, which contains at least some hydrated calcium oxide, with carbonate ions in an aqueous medium for preparing precipitated calcium carbonate. The calcium carbonate is separated from the suspension and subjected to further treatment for preparation of the desired end product. The invention is characterized in that at least 80 % of the particles of the hydrated calcium oxide have a particle size of less than 3 μm and the reaction is allowed to proceed without mixing the reaction mixture. When a pigment suitable for paper coating, having a particle size of 0.2 to 0.4 μm, is to be prepared, the carbonation reaction is allowed to continue for 20 to 25 minutes before it is interrupted in an impact mixer (12).</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Process and apparatus for preparing calcium carbonate

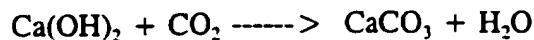
5 The present invention concerns a process in accordance with the preamble of claim 1 for preparing calcium carbonate, in particulate calcium carbonate having a controlled crystal structure.

10 According to such a process, calcium carbonate is produced by reacting a calcium oxide-based raw material, which contains at least some hydrated calcium oxide (i.e. calcium hydroxide), with carbonate ions in an aqueous medium in order to produce an aqueous suspension containing calcium carbonate, and then separating the precipitated calcium carbonate from the suspension and subjecting it to post-treatment in order to produce the desired end product. When the carbonate ions are derived from sodium carbonate, sodium hydroxide can be recovered from the suspension, if desired.

15 The present invention also concerns an apparatus according to the preamble of claim 21 for preparing calcium carbonate.

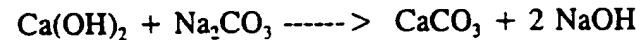
20 Synthetic or industrial or precipitated calcium carbonate, which in the following will be referred to by the abbreviation PCC (Precipitated Calcium Carbonate) is becoming more and more used as a filler and mixing pigment in the chemical, pharmaceutical, polymer and paper industry and as a coating pigment for paper. With an increasing use and a larger number of applications more stringent requirements are also set on the properties of the product. The most important product properties of synthetic calcium 25 carbonate for different applications are related to the crystalline form and crystal dimensions of the crystallized product. Furthermore, for many applications it is preferable to have a narrow crystal size distribution, i.e. the crystals should be of the same size.

30 Calcium carbonate for the paper industry is most commonly prepared in plants known as satellite plants, i.e. facilities at a paper mill site. The process of these plants is based on the following reaction:



5 Thus, an aqueous suspension (lime milk) containing slaked lime is carbonated with carbon dioxide from, for example, flue gases or off-gases from lime burning kilns. The product obtained comprises calcium carbonate and water.

10 Before the chlorine-alkali-process based on electrolysis became common, sodium hydroxide was prepared by causticizing of soda and lime by the well-known causticizing reaction:



15 In addition to sodium hydroxide, also (precipitated) calcium carbonate was then obtained.

20 15 For ecological reasons, the global production of chlorine and caustic soda is in imbalance; the use of chlorine is steadily declining and the use of caustic soda constantly increasing by and by. As far as the production of sodium hydroxide is concerned, this development has diminished the economical importance of the chlorine-alkali-process and, correspondingly, made the causticizing reaction more interesting. Thus, causticizing processes have been built in the recent years in areas, wherein, for example, natural soda (sodium carbonate) is available. However, in all of these processes, lime is constantly circulating via the mesa oven and the only product obtained is lye (caustic soda).

25 20 In summary, it can be stated that there is a need for a combination of carbonation and causticizing so as to provide for simultaneous production of caustic soda and calcium carbonate by one process. However, in practice, the above-described process combination has so far not been successfully achieved to produce high-quality 30 precipitated calcium carbonate (PCC) suitable for use as a filler or pigment.

In all processes, wherein a crystallizing product is being produced, the provision of the

slaking is, however, preferred for PCC processes, because it will provide a means for easy separation of sand and coarse particles from the dilute lime milk by the use of a hydrocyclone.

5 It is an object of the present invention to eliminate the problems related to the prior art and to provide an entirely novel solution for preparing calcium carbonate.

10 The invention is based on the idea that it is possible to prepare finely divided calcium carbonate having uniform particles sizes by carbonation or causticizing, if also the particles of the calcium hydroxide are of uniform size and, preferably, only 50 times greater than the calcium carbonate particles. Preferably, according to the invention, at least about 80 % of hydrated calcium oxide particles, which are reacted with the carbonate ions, are smaller than about 3 μm .

15 Another characteristic feature of the invention is that the reaction between the calcium hydroxide and the carbonate ions is allowed to take place essentially without any mixing of the reaction mixture until the desired particle size of the calcium carbonate is achieved. The reaction is then interrupted after a predetermined time by subjecting the reaction mixture to strong mixing forces. The length of the selected time is determined by the desired size and form of the produced particles.

20 In particular, the process according to the invention is mainly characterized by what is stated in the characterizing part of claim 1.

25 The apparatus according to the invention is, again, characterized by what is stated in the characterizing part of claim 21.

Some features of the apparatus are disclosed in the characterizing parts of dependent claims 22 to 26.

30 According to a preferred embodiment of the invention, PCC suitable for paper coating is produced, the particle or granular size of which is in the range: $0.2 \mu\text{m} < \varnothing < 0.4$

After a preselected time the carbonation reaction is interrupted by mixing the mixture so intensively that at least a part of the calcium carbonate crystals formed in the reaction mixture are broken up. Preferably this interruption is effected with an efficient mixer by using strong turbulence and impact and shearing forces. It is particularly preferred to use an impact mixer for this purpose as well.

5 The preparation of a calcium carbonate product suitable for use as a paper filler takes some 15 to 35 minutes, typically about 20 to 30 minutes. It has been found that when the mixture is disturbed before the end of said time and before the crystals have grown to the size 0.2 to 0.4 μm , there are present abundantly crystals, which are smaller than 10 0.2 μm in particle size and which are not preferred for the preparation of paper pigments.

15 The term "impact mixer" as used in the present context denotes an apparatus equipped with rotating rotors provided with plate-like impact stops which generate an over-sized shear force (after the impact) which causes the liquid and suspension to flow in the direction of the centrifugal force from the impact stops on the inner mixing rotor to the impact stops of a concentrical outer roter, rather large shear forces being directed 20 towards the mixture when it flows from one impact stop to another. These shear forces are caused by the fact that the vanes of successive rotors have different speeds and rotating directions. An apparatus of this kind uses vanes or plates which are either radial or slightly inclined in the rotational direction. An impact mixer will make it possible to perform uniform mixing, and the shearing force resulting from the impacts between the solid matter and the solid impact surfaces is more even and uniform.

25 statistically calculated. than in nother types of mixers. Typically over 95 % of the material flux obtains almost 100 % of the maximum impact energy and only 5 to 10 % gets less than 60 % of the maximum impact energy. The variation of the intensity of the mixing turbulence is many times greater for all other types of mixers, even for the dissolver type "high-shear" mixers. Because of the afore-mentioned reasons, renewed 30 disintegration of the aggregates and flocs formed is almost total in comparison to a conventional mixer.

After a preselected time the carbonation reaction is interrupted by mixing the mixture so intensively that at least a part of the calcium carbonate crystals formed in the reaction mixture are broken up. Preferably this interruption is effected with an efficient mixer by using strong turbulence and impact and shearing forces. It is particularly preferred to use an impact mixer for this purpose as well.

5 The preparation of a calcium carbonate product suitable for use as a paper filler takes some 15 to 35 minutes, typically about 20 to 30 minutes. It has been found that when the mixture is disturbed before the end of said time and before the crystals have grown 10 to the size 0.2 to 0.4 μm , there are present abundantly crystals, which are smaller than 0.2 μm in particle size and which are not preferred for the preparation of paper pigments.

15 The term "impact mixer" as used in the present context denotes an apparatus equipped with rotating rotors provided with plate-like impact stops which generate an over-sized shear force (after the impact) which causes the liquid and suspension to flow in the direction of the centrifugal force from the impact stops on the inner mixing rotor to the impact stops of a concentrical outer roter, rather large shear forces being directed 20 towards the mixture when it flows from one impact stop to another. These shear forces are caused by the fact that the vanes of successive rotors have different speeds and rotating directions. An apparatus of this kind uses vanes or plates which are either radial or slightly inclined in the rotational direction. An impact mixer will make it possible to perform uniform mixing, and the shearing force resulting from the impacts between the solid matter and the solid impact surfaces is more even and uniform.

25 statistically calculated. than in nother types of mixers. Typically over 95 % of the material flux obtains almost 100 % of the maximum impact energy and only 5 to 10 % gets less than 60 % of the maximum impact energy. The variation of the intensity of the mixing turbulence is many times greater for all other types of mixers, even for the dissolver type "high-shear" mixers. Because of the afore-mentioned reasons, renewed 30 disintegration of the aggregates and flocs formed is almost total in comparison to a conventional mixer.

5 The impact mixer can also be used for slaking of calcium oxide, as the detailed description given below will show. According to one embodiment, calcium oxide containing raw material containing at least a part of hydrated calcium oxide, is produced by grinding calcium oxide first to a granular size of less than 200 times the diameter, which is set as the upper limit for 80 % of the crystals of the slaked lime. The calcium oxide is slaked by mixing it in water, the mixture formed by the calcium oxide and water being subjected to strong shear forces during mixing.

10 When a narrow crystalline size distribution of the carbonate product is sought, the crystallization reaction of the CaCO_3 is initiated, continued and finished on the surface of each uniformly sized $\text{Ca}(\text{OH})_2$ particle as simultaneously as possible by initiating the reaction with rapid turbulent mixing (e.g. by using an impact mixer), the reaction is continued by leaving the mixture essentially unmixed during the reaction time in a tank, wherein the particles can be formed in as homogeneous conditions as possible, and 15 after the reaction time a turbulent postmixing is carried out in order to avoid smaller CaCO_3 particles than desired.

20 According to one preferred embodiment, the process according to the invention is implemented as a causticizing process, which comprises the simultaneous preparation of both paper coating grade PCC (rhombic calcite) and a ready-to-use caustic soda solution for the process of a pulp mill. According to this embodiment the carbonate ions are brought to the reaction with calcium hydroxide in the form of, e.g., a sodium carbonate solution. Alternatively, a part — even the main part — of the carbonate ions can be introduced into the process with flue gas or as pure carbon dioxide and 25 preferably only the initial nucleation is carried out by soda and the obtained caustic soda is left in solution as a dispersion adjuvant, whereby filtration only comprises concentration of the slurry, if needed.

30 The carbon dioxide obtained from flue gases can preferably also be introduced by first binding it to NaOH to form Na_2CO_3 , and then contacting this matter with $\text{Ca}(\text{OH})_2$. The formed NaOH or a part thereof is returned to the gas absorber.

The NaOH produced by the invention can be used as such in a pulp mill or it can be sold for other purposes after concentration, e.g., by evaporation. .

5 The process equipment described makes it also possible to regulate the ratio between the formed calcium carbonate and NaOH by feeding carbon dioxide containing gas or pure carbon dioxide into the impact mixer of the process, if the need for caustic soda is smaller than the equivalent amount of the corresponding calcium carbonate. The gas feed to said impact mixer is facilitated by the fact that the operational space of the mixer is mainly empty during the use of the mixer. By varying the component ratios of 10 the mixture the concentration of the NaOH solution can be set at 6 to 15 %, which means that it is ready to be used in the processes of most pulp mills.

15 The present invention provides considerable advantages. Thus, the process has been designed so that the PCC can be prepared as easily as possible and by using as simple equipment as possible. The process and the apparatus according to the invention are suitable for forming calcium carbonate both by the causticizing reaction and by flue gas carbonation, while ensuring in both cases an extremely narrow crystal size distribution and the means for regulating it. The process according to the invention excellently fulfilled the set requirements during our tests, but surprisingly it has been found that 20 the process is suitable for controllable preparation of other crystalline forms of calcium carbonate (aragonite/calcite) and other crystalline sizes thereof by the causticizing process as well. This is also possible when the preparation process employs gas carbonation in addition to the caustification process or instead of it. The crystalline form of the produced calcium carbonate is preferably controlled by regulating the 25 process temperature to below +42 °C. when calcite crystals are to be prepared, and above +43 °C, when aragonite crystals are produced.

30 Next, the invention will be described in more detail with the aid of the attached drawing and photographs. whereat Figure 1 indicates the process scheme for a preferred embodiment of the invention, Figures 2 to 8 comprise electron microscope micrographs taken of the reaction mixture at different points of time (the times are calculated on basis of the premixing).

The most important steps of our invention are the slaking of the lime, carbonation, the interruption of the carbonation and the filtration, which are described in the following with reference to Figure 1.

5 1. Slaking of lime

Slaking of lime for the causticizing (and/or gas carbonation) is preferably continuously performed, depending on the need of the slaked lime, a relatively short period of time before the initiation of the carbonation. The slaking of the lime comprises the following 10 steps:

The starting material, CaO, is fed via the feed hopper 1 to pregrinding 2, for example to a vibratory cone crusher (crushing ratio preferably 2 to 8, in particular about 5), which is used for grinding the CaO to desired fineness, with a maximum granular size 15 of preferably 5,000 to 15,000, in particular < 10,000, times the aimed crystal size of the end product carbonate.

The preground CaO is fed with water to, for instance, an impact mixer/slaking apparatus 3 of the ATREX type, which within a short residence time (preferably < 1 second) subjects each unit volume of the components which are to be mixed to a spread 20 of shear forces of essentially uniform intensity under strong turbulence. According to our investigations, of the calcium hydroxide crystals which are generated in this way, at least 80 % have a diameter which is less than 1/200 of the maximum size of the preground CaO even after 24 hours from the initiation of crystallization. Since the 25 solubility of slaked lime in water is only about 2 g/liter, the size of the calcium hydroxide crystal means, in the present context, the size of the insoluble solid particle in the aqueous suspension, as expressed by an approximate value for its mean diameter.

The calcium oxide-based aqueous slurry obtained from the slaking (lime milk) is 30 pumped 4 to an intermediate tank 5.

The sodium carbonate solution used for carbonation can be prepared in the same

apparatus as the calcium carbonate. The break tank for the aqueous solution of sodium carbonate is given the reference number 6.

2. The carbonization reaction

5

Because it is an aim to achieve as small and uniformly sized crystals of slaked lime as possible, which crystals can then be used as a raw material for the carbonate to be prepared, the CaO has to be preground, slaked as soon as possible and reacted with soda (and/or carbon dioxide) so that the calcium hydroxide crystals formed do not have time to grow too big or to agglomerate.

10

The crystallization of CaCO_3 is initiated as simultaneously as possible throughout the whole process batch by bringing the surfaces of the $\text{Ca}(\text{OH})_2$ particles and the Na_2CO_3 solution (and/or CO_2) in immediate mutual contact by means of efficient initial mixing.

15

Preferably, this is again achieved with the help of an ATREX type impact mixer 9 or a similar apparatus, for which it is typical that when the mixer is treating in its mixing chamber in comparison to its total volume very small amounts of mixture at a time and very quickly (residence time < 1 second), the vanes of the mixing rotors of the impact mixer subjecting each particle with a probability great enough to the necessary mixing energy for immediately initiating the carbonation reaction.

20

By using the dosing equipment or batcher of the premixer (pumps 7, 8) it can be ensured that the weight ratios of the substances needed for the reaction are proper, and also the dosing of the gas to the reaction can be carried out in connection with the premixing. The gas dosing is not shown in Figure 1. A strong turbulence during premixing ensures simultaneous initiation of the growth of carbonate crystals.

25

30

The premixing produces a reaction mixture, which contains hydratated calcium oxide stemming from the calcium oxide-based starting material and carbonate ions. It is fed into the PCC reactor 11 from above. The reactor comprises a cylindrical tank whose longitudinal axis is vertical and lower end is conical.

The reaction time in the reactor 11 depends on the desired crystal size of the final product; for coating PCC prepared from $3 \mu\text{m} \varnothing \text{ Ca(OH)}_2$ it takes some 20 to 25 minutes to prepare CaCO_3 with a diameter in the range of $0.2 \mu\text{m} < \varnothing < 0.4 \mu\text{m}$. According to the invention, the mixture is essentially not mixed after the initial mixing.

5 Instead, the carbonate crystals are allowed to form without disturbance as the surface layer of the Ca(OH)_2 particles continuously reacts with the surrounding soda solution until, when the whole hydroxide particle has reacted, the carbonate crystals formed on its surface have reached the desired size. If the reaction is allowed to proceed long enough the ready carbonate crystal will separate from each other, while the other

10 product produced by the process, viz. NaOH , works as a dispersion medium and keeps the formed crystals separated from each other.

The tests we have carried out clearly show that the mixture will form a gel after about 5 minutes of reaction (cf. the example described below), when the carbonate crystals formed on the surface of the hydroxide "parent particles" have grown so large that they fill up the spaces between the Ca(OH)_2 particles, thus increasing the viscosity of the mixture (later: viscous reaction stage). The surprising finding that the carbonate crystal disperse after the "parent particles" have been wholly consumed, when the reaction proceeds far enough, manifests itself in our test in that the mixture becomes liquid.

20 This phenomenon has not been observed or correctly understood in the prior art processes, because, as far as we are aware, the prior art has attempted to prevent this "gelling" by continuing the mixing during the whole reaction, a part of the freshly formed carbonate crystals being continuously broken, which enlarges the crystal size distribution to include more finely divided material. Thus, the possibilities of producing

25 easily filtered CaCO_3 crystals, which are uniform in particle size, are lost.

The crystalline form of the prepared calcium carbonate depends on the temperature of the crystallization. Calcite crystals are formed at temperatures below 42.5°C and typically more oblong aragonite crystals at higher temperatures. In order to control the crystalline form, the apparatus 11 is equipped with heat regulation means. This is important also for the reason that the use of small Ca(OH)_2 particles and the efficient

initial mixing by using an impact mixer will increase the heat generation during the process.

3. Interruption of carbonation

5

After the desired reaction time the reaction mixture is removed from the reactor 11 and conducted to a mixer 12 for interruption of the carbonation. This measure, which is also called post-mixing, is preferably carried with an impact mixer 1 to 4 times, because it is possible by the post-mixing to react unreacted $\text{Ca}(\text{OH})_2$ with the already existing CaCO_3 particles. By selecting the point of time for the post-mixing, it is possible to regulate the form and maximum size of the produced crystals. In this way the formation of under-sized carbonate crystals generated by reaction residues can be avoided. Based on our test results and also pursuant to a theory, known as Kormogorov's and Hinze's law, which relates to the mixing length of turbulence, the post-mixing performed by an impact mixer helps to keep the crystal size distribution narrow because the mixing only increases the size of such particle agglomerates which it is incapable of disintegrating. In connection with the post-mixing, the reaction can be enhanced by dosing carbon dioxide into the mixture. if the mixture does not contain enough dissolved free soda or if the NaOH concentration in the mixture becomes too high for the causticizing reaction to proceed in the desired direction.

20

4. Filtration

25

From the mixer 12 the mixture is pumped 13 to a tank 15, to which pressurized air is pumped from a storage tank 14. The mixture is conducted with the pressurized air to a filtration unit 16. The filtration can be carried out by using a cassette-type pressure filter 16 provided even with very fine filtration cloths. because the size distribution of the CaCO_3 crystals produced is so narrow that the cloths do not form dense overlapping plates. but the NaOH filtrate can always be pressed through them.

30

It is preferred to carry out the filtration by pressurization using pressurized air in order to avoid excessive dilution of the filtrate, i.e. usually the aqueous sodium hydroxide

solution.

The sodium hydroxide solution is recovered and conducted to the vessel 20.

5 The pressure filter is washed with water and the PCC slurry is conducted to the intermediate storage tank 21, from which it can be further conducted to storage tank 23. For the preparation of PCC powder, at least a part of the slurry can also be dried in a dryer 24.

10 The rinsing water, which contains some PCC and sodium hydroxide is recirculated to the slaking of calcium oxide.

15 In the following, the process according to the invention and the process apparatus preferably used for implementing the process will be examined in more detail with the aid of a working example and the attached micrographs relating to the simultaneous preparation of coating PCC and NaOH, which is the embodiment most studied by us.

Example

20 The following test shows the working of the invention on laboratory scale.

Test arrangements:

25 1. Slaking of lime: CaO, Ø 10 mm, was preground in a vibratory cone crusher to a diameter of < 2 mm. The slaking was carried out in an ATREX-mixer at a temperature of 75 to 80 °C at a solids content of 12 %. The Ca(OH)₂ was allowed to post-slake in a tank for about 20 h.

30 2. The Na₂CO₃ was dissolved in water at a temperature > 30 °C, in order to prepare a saturated solution with a concentration of about 32 %.

3. The causticizing process was carried out in a laboratory at the Technical University

of Helsinki, equipped with an electron microscope for monitoring the progress of the process. However, at the laboratory, no ATREX mixer was available for achieving the initial mixing. Because the amount of mixing components was small (Ca(OH)₂ mixture, 5 50 g, and Na₂CO₃ solution 23.5 g) the process could, however, be initiated simultaneously enough throughout the whole mixture by using a laboratory mixer for the initial mixing of the components.

10 4. The temperature during the whole reaction stage was maintained at < 30 °C. The process components were inspected with an electron microscope after 5, 15, 19, 22, 25, 29, 39 and 60 minutes from the start of the causticizing reaction. Before the reaction, the Ca(OH)₂ raw material was also inspected with the aid of an electron microscope.

15 Test results:

The main stages of the process:

20 Figure 2 — the Ca(OH)₂ particles are relatively separate, granular size about 2 - 4 μm Ø.

Figure 3 — after about 5 minutes the mixture begins to arrange as a uniform viscous mixture with detectable particles having a Ø of about 2 μm .

25 Figure 4 — about 25 minutes: The particle sizes are 0.2 - 0.4 μm , post-mixing is initiated.

30 The electron microscope micrographs of the intermediate stage of the reaction indicate the rapid change of the composition of the reaction mixture:

Figure 5 — about 15 minutes: The particles are still distinguishable as spherical particles, which have a rough surface and are adhering to each other: the viscosity of the mixture is high.

Figure 6 — about 19 minutes: A uniform gelled mass, with lumps of a size of about 2 μm Ø.

Figure 7 — about 22 minutes: A uniform gelled mass, with hardly any distinguishable particles.

5 Electron microscope micrographs of the situation which will prevail when the reaction is allowed to continue even after 30 minutes.

Figure 8 — about 39 minutes: Rod-shaped crystals, \varnothing 1 - 2 μm , length 5 - 10 μm . are beginning to form in the gel (Figure 8).

10 Figure 9 — about 43 minutes: The crystals which can be seen in the previous micrograph disintegrate

Figure 10 — about 60 minutes: CaCO_3 is primarily in soda solution in the form of rod-shaped crystals with lengths in the range from 5 to 20 μm and having a diameter of 2 μm . and in the form of granular crystals with a diameter of 0.1 to 1.0 μm .

15 The test shows that when the caustification process is interrupted according to the invention, e.g. during the preparation of coating PCC (0.2 to 0.4 μm \varnothing) 15 to 25 minutes from the initiation of the reaction with the aid of efficient ATREX mixing, the desired end result is obtained by homogenization of the mixture, as the crystals formed in the gel are dispersed by the NaOH formed and when the loose agglomerates in the 20 gel are broken up.

25 The test further showed that during the high-viscosity stage of the reaction, i.e. within about 5 to 15 minutes from the beginning of the reaction, mixing of the mixture is not necessary. From this it can be inferred that, in addition to the great energy consumption of mixing, it would not be advantageous to mix the mixture also because mixing of the forming $\text{NaCO}_3 + \text{Ca}(\text{OH})_2$ gel with the generated NaOH would slow down the growth of the CaCO_3 crystals to the desired size and therefore leave too much extremely small PCC crystals in the product, which will make filtering more difficult.

30 It also appeared that the crystals become oblong in the gel unless the reaction is interrupted by means of an efficient post-mixing. This confirms the fact that the process according to the invention can be regulated by timing the post-mixing so that PCC

crystals of varying shapes and sizes are produced at the desired size distribution.

Claims:

1. A process for preparing calcium carbonate, according to which process

- a calcium oxide raw material, which contains at least some hydrated calcium oxide, is reacted with carbonate ions in an aqueous medium in order to prepare calcium carbonate.
- the initial concentrations of calcium oxide, hydrated calcium oxide and of the carbonate ions is being maintained so high that calcium carbonate is precipitated into the medium, whereby an aqueous calcium carbonate-containing suspension is being formed, and
- the precipitated calcium carbonate is separated from the suspension and subjected to further treatment for preparation of the desired end product.

characterized in that

- at least about 80 % of the particles of the hydrated calcium oxide subjected to the reaction have a particle size of less than about 3 μm ,
- the reaction is allowed to proceed essentially without mixing of the reaction mixture containing hydrated calcium oxide and carbonate ions, and
- the reaction is interrupted after a predetermined time by applying mixing forces to the reaction mixture.

20

2. The process according to claim 1, wherein the hydrated calcium oxide particles brought to the causticizing reaction have a particle diameter which, at the most, is 50 times the maximum particle size of the produced calcium carbonate.

25

3. The process according to claim 1 or 2, wherein calcium carbonate is prepared, mainly having a particle size of 0.2 to 0.4 μm .

30

4. The process according to claim 3, wherein at least about 80 % of the particles of the hydrated calcium oxide subjected to the reaction have a particle size of less than 10 μm .

5. The process according to any of claims 1 to 4, wherein the carbonation reaction is

interrupted by mixing the mixture so vigorously that at least a part of the calcium carbonate particles formed into the reaction mixture are disintegrated.

5 6. The process according to claim 5, wherein the mixture is mixed with an impact mixer.

10 7. The process according to any of claims 1 to 6, wherein, for preparing calcium carbonate products, such as calcium carbonate suitable for paper coating, with a narrow particle size distribution, the reaction mixture is subjected to a mixing action, which disintegrates CaCO_3 crystals at the earliest after at least 15 minutes from the initial mixing of the components or when the mixture during the course of the reaction has become plasticized again.

15 8. The process according to any of the preceding claims, wherein the reaction mixture containing hydrated calcium oxide and carbonate ions is formed in the initial stage of the process by mixing together in an impact mixer an aqueous suspension containing a calcium oxide-based raw material and an aqueous suspension containing carbonate ions.

20 9. The process according to any of the preceding claims, wherein the carbonate ions are brought into the reaction mixture in the form of an aqueous solution of sodium carbonate.

25 10. The process according to claim 9, wherein the carbonate ions are also introduced into the reaction mixture in the form of carbon dioxide.

11. The process according to claim 10, wherein carbon dioxide is brought into the reaction mixture during the initial mixing stage in the form of pure carbon dioxide gas or in the form of a gas mixture containing carbon dioxide, said gas or gas mixture being fed into the mixing zone of the impact mixer.

30 12. The process according to claim 10 or 11, wherein carbon dioxide is introduced into the reaction mixture during the interruption of the reaction in the form of pure carbon

dioxide gas or as a gas mixture containing carbon dioxide, said gas or gas mixture being fed into the mixing zone of the impact mixer.

5 13. The process according to any of claims 1 to 7, wherein the carbonate ions are introduced into the reaction mixture in the form of carbon dioxide.

14. The process according to any of the previous claims, wherein the starting material containing at least partially hydrated calcium oxide is produced by

10 - grinding calcium oxide into a particle size which is less than 200 times the maximum diameter for 80 % of the crystals of the slaked lime, and

- the calcium oxide is slaked by mixing it with water, strong shear forces being applied to the mixture formed by calcium oxide and water.

15 15. The process according to claim 14, wherein the calcium oxide is slaked by mixing it with water in an impact mixer.

16. The process according to claim 14 or 15, wherein the calcium oxide is ground to the desired granular size in a vibratory cone crusher.

20 17. The process according to any of claims 14 to 16, wherein the calcium oxide is ground to a maximum particle size of 2 mm.

25 18. The process according to claim 1, wherein the crystal size of the calcium carbonate produced is controlled by adjusting the temperature to below +42 °C, when calcite crystals are produced, and to above +43 °C, when aragonite crystals are produced.

19. The process according to claim 9, wherein the concentrations of the starting materials are such that a solution of NaOH is produced by the causticizing reaction, which has a concentration of 6 % to 15 %.

30

20. The process according to any of the preceding claims, wherein the calcium carbonate is filtered on a pressure filter.

21. An apparatus for preparing calcium carbonate, which apparatus comprises

- a reaction tank (11), wherein a calcium oxide-based raw material, which contains at least some hydrated calcium oxide, can be reacted with carbonate ions in an aqueous medium in order to produce calcium carbonate,
- feeding means (9, 10) connected to the reaction tank for the calcium oxide-based starting material and for an aqueous solution containing carbonate ions, and
- discharge means (12, 13) connected to the reaction tank for removing the calcium carbonate product from the tank,

10 characterized in that

- said feeding means are connected to an impact mixer (9), wherein the calcium oxide-based starting material and the carbonate ions containing aqueous solution can be mixed together before they are fed into the reaction tank (11).

15 22. The apparatus according to claim 21, wherein the impact mixer is provided with a feed nozzle for carbon dioxide gas or gas containing carbon dioxide, in order to bring carbon dioxide in contact with the aqueous slurry of the calcium oxide-based raw material.

20 23. The apparatus according to claim 21 or 22, wherein an impact mixer (12) is connected to the discharge means for interruption of the reaction between the hydrated calcium oxide and the carbonate ions.

24. The process according to any of claims 21 to 23, which further comprises a slaking
25 unit (1 - 4) for calcium oxide, which unit is connected to the feeding means of the
reaction tank and intended for preparation of an aqueous slurry containing hydrated
calcium oxide. characterized in that said unit is formed by a crusher (2) for
disintegration of calcium oxide and an impact mixer (3) connected to the outlet of the
crusher, wherein the disintegrated calcium oxide can be brought into contact with
30 water.

25. The apparatus according to claim 24, wherein the crusher is a vibratory cone

crusher.

26. The process according to claims 21 to 25, wherein the outlet of the impact mixer (12) is connected to a pressure filter (16), which can be used for separating the solid matter from the aqueous slurry.

1/4

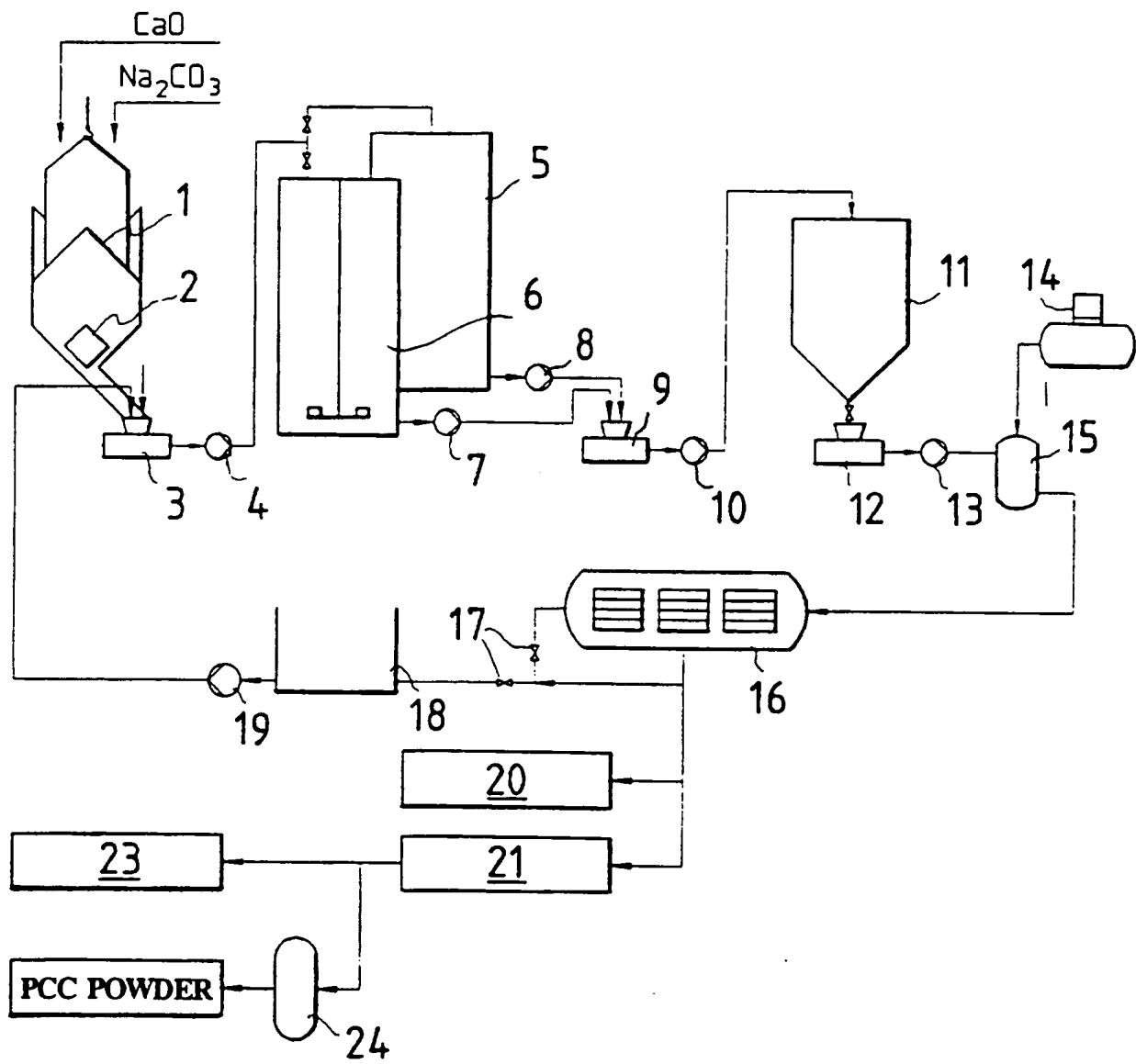


Fig. 1

2/4

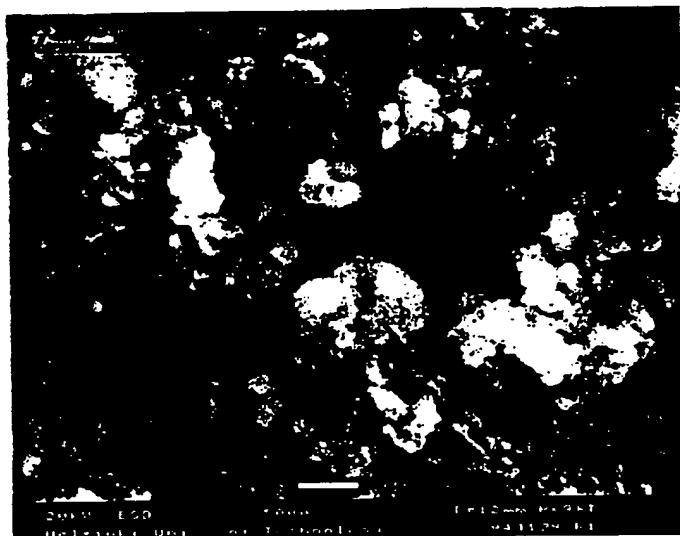


FIG. 2

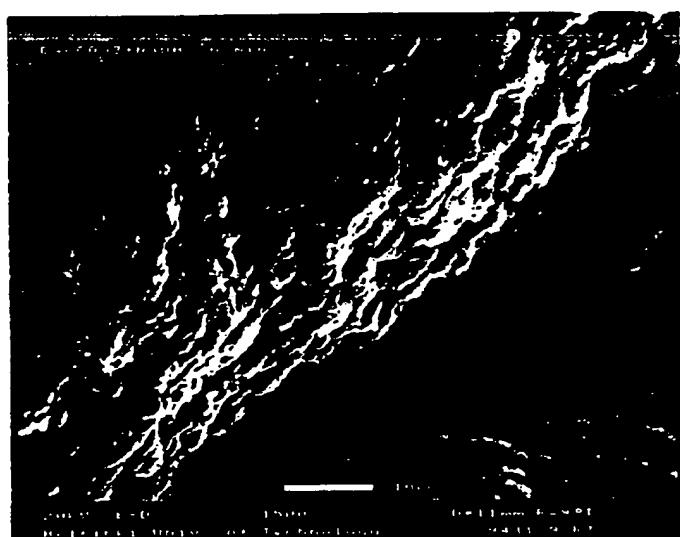


FIG. 3

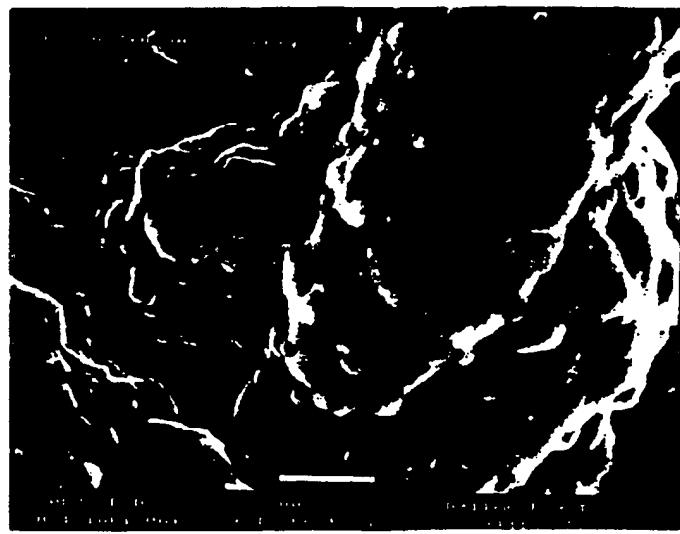


FIG. 4

3/4

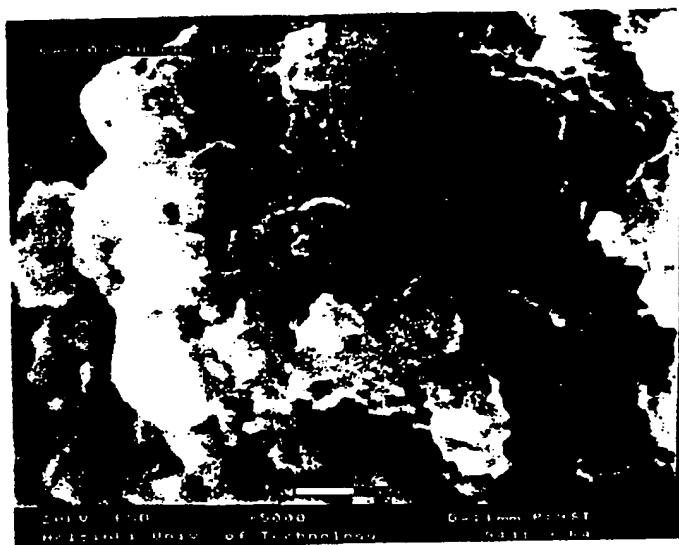


FIG. 5

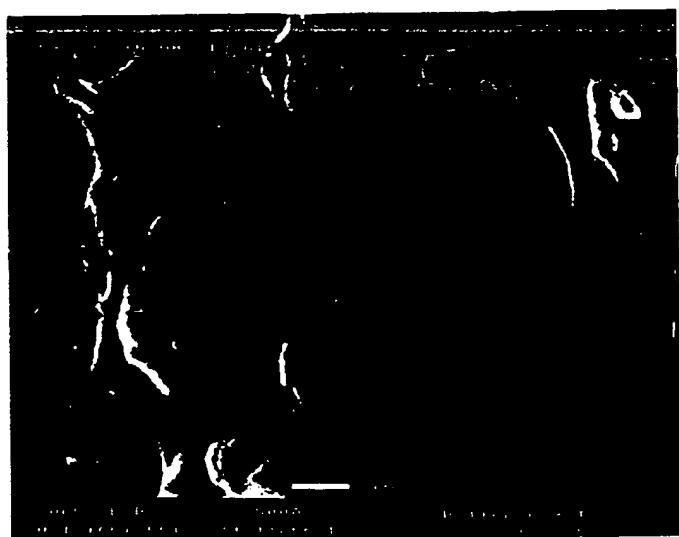


FIG. 6

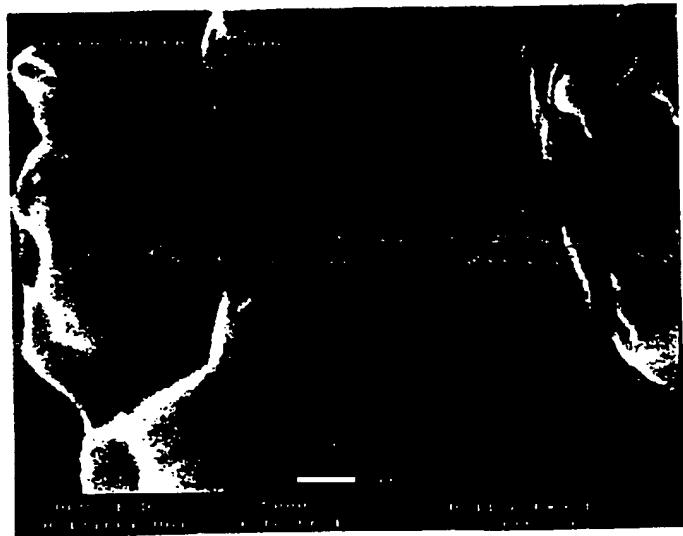


FIG. 7

SUBSTITUTE SHEET (RULE 26)

BEST AVAILABLE COPY

4/4

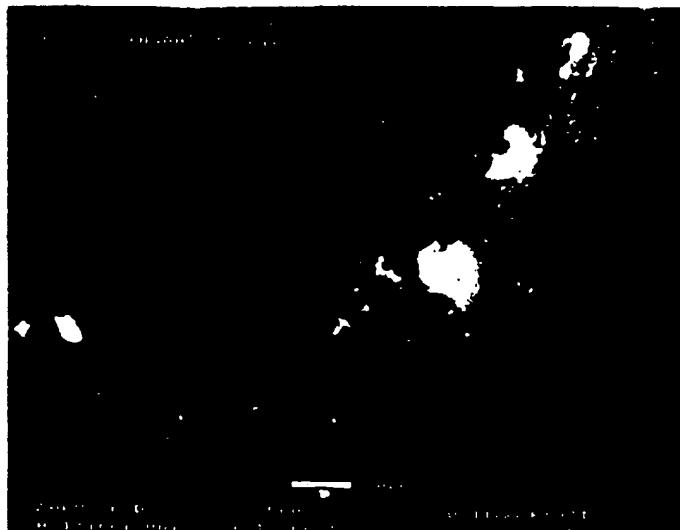


FIG. 8

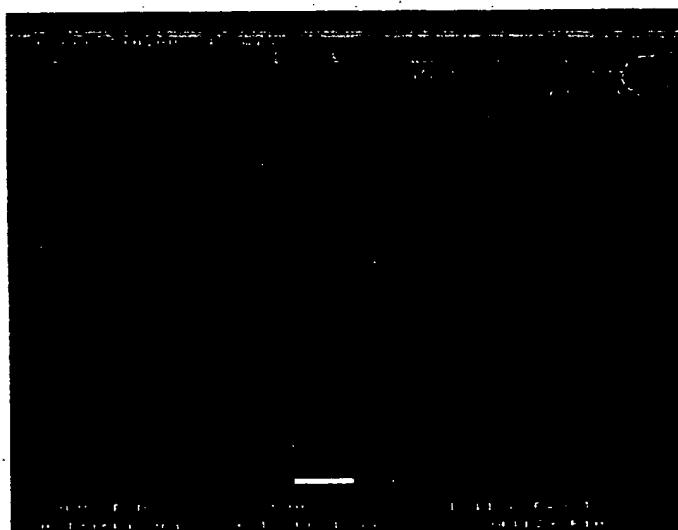


FIG. 9



FIG. 10

SUBSTITUTE SHEET (RULE 26)

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

International application No

PCT/FI 96/00058

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C01F 11/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	WO 9312038 A1 (ADLER, PAUL, E.), 24 June 1993 (24.06.93) --	1-26
A	US 5342600 A (BLEAKLEY ET AL), 30 August 1994 (30.08.94) --	1-26
A	US 5364610 A (MERRIS, JR.), 15 November 1994 (15.11.94) -- -----	1-26

 Further documents are listed in the continuation of Box C. See patent family annex

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "B" earlier document but published on or after the international filing date
- "C" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "D" document referring to an oral disclosure, use, exhibition or other means
- "E" document published prior to the international filing date but later than the priority date claimed
- "F" later document published after the international filing date but earlier than the priority date claimed, which contains information which, in the opinion of the examiner, is of relevance to the examination of the application
- "G" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "H" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "I" document member of the same patent family

Date of the actual completion of the international search 17 April 1996	Date of mailing of the international search report 02 -05- 1996
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. + 46 8 666 02 86	Authorized officer Britt-Marie Lundell Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/04/96

International application No.

PCT/FI 96/00058

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A1- 9312038	24/06/93	AU-A-	3277193	19/07/93
		CA-A-	2125695	24/06/93
		EP-A-	0616602	28/09/94
		FI-A,D-	942797	25/07/94
		NO-A,D-	942218	28/07/94
		US-A-	5205493	27/04/93
<hr/>				
US-A- 5342600	30/08/94	AT-T-	114143	15/12/94
		AU-B-	649721	02/06/94
		AU-A-	8526291	28/04/92
		CA-A-	2087857	28/03/92
		DE-D,T-	69105183	24/05/95
		EP-A,A,A	0480587	15/04/92
		SE-T3-	0480587	
		ES-T-	2064047	16/01/95
		GB-A,B-	2248229	01/04/92
		JP-T-	6501235	10/02/94
		WO-A,A-	9206038	16/04/92
<hr/>				
US-A- 5364610	15/11/94	CA-A-	2125846	16/12/94
		FI-A,D-	942815	16/12/94
		SE-A,D-	9401906	16/12/94
<hr/>				